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Energetic Component Treatability Study

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P. D. Gildea, S. L. Brandon, B. G. Brown, B. L. Haroldsen, J. Lipkin, W. C. Replogle, T. J. Shepodd, D. V. Zanini

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Energetic Component Treatability Study

by

Patrick D. Gildea, Stephen L. Brandon, Bert G. Brown, Brent L. Haroldsen,
Joel Lipkin, William C. Replogle, Timothy J. Shepodd, David V. Zanini

Sandia National Laboratories

Albuquerque, New Mexico

Livermore , California

Abstract

The effectiveness of three environmentally sound processes for small energetic component disposal was examined experimentally in this study. The three destruction methods, batch reactor supercritical water oxidation, sodium hydroxide base hydrolysis and calcium carbonate cookoff were selected based on their potential for producing a clean solid residue and a minimum release of toxic gases after component detonation. The explosive hazard was destroyed by all three processes. Batch supercritical water oxidation destroyed both the energetics and organics. Further development is desired to optimize process parameters. Sodium hydroxide base hydrolysis and calcium carbonate cookoff results indicated the potential for scrubbing gaseous detonation products. Further study and testing are needed to quantify the effectiveness of these latter two processes for full-scale munition destruction.

The preliminary experiments completed in this study have demonstrated the promise of these three processes as environmentally sound technologies for energetic component destruction. Continuation of these experimental programs is strongly recommended to optimize batch supercritical water oxidation processing, and to fully develop the sodium hydroxide base hydrolysis and calcium carbonate cookoff technologies.

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1.0 Executive Summary

Small energetic components such as detonators and actuators commonly used in weapon systems are generally inventoried in large numbers. These components contain a variety of hazardous, reactive materials including, toxic lead and mercury compounds and can represent a serious disposal problem. Traditional disposal methods such as open burning, open detonation and incineration are limited because of environmental concerns related to atmospheric release of toxic gases and soil contamination by heavy metals.

The study described in this report was undertaken to explore the effectiveness of alternative, environmentally sound options for disposal of small energetic components. All of the tests were performed using MC1061 and MC1981 hot wire actuators. Each actuator contains 250 mg lead styphnate and is about 0.5 inches in diameter and 1.0 inches long. The small size of individual components enabled us to carry out the experiments at the bench scale under laboratory conditions. The following three processes were chosen based on their potential for producing a clean, solid residue and a minimum release of toxic gases after detonation.

- Supercritical water oxidation (SWCO) batch reactor
- Sodium hydroxide solution (NaOH) scrubbing (base hydrolysis), and
- Calcium carbonate ($CaCO_3$), limestone, cookoff

Each of these concepts has specific application potential for use on shaped charges, component assemblies or chemical filled rounds. None of the methods requires component disassembly prior to application, thus enhancing personnel safety.

Supercritical water oxidation At supercritical water conditions (374 °C, 3200 psi), explosive compounds can be efficiently oxidized to innocuous compounds. Batch reactor processing was chosen because it offers the advantage of testing several components simultaneously without disassembly. Up to eight actuators are placed in the reactor with water and oxidizer. As the reactor is heated to supercritical conditions, the primary explosive detonates at about 275 °C, the autoignition temperature for lead styphnate. After detonation, the organic constituents and detonation products are destroyed by the oxidizer in the reactor as it reaches supercritical conditions.

Sodium hydroxide base hydrolysis Base hydrolysis employing NaOH solution is commonly used for desensitization and disposal of energetic materials and for scrubbing acid gases produced during incineration. This process is employed by electrically detonating the actuator while immersed in NaOH solution in a pressure vessel. Using this method, detonation products (solid residue and gases) are contained and hydrolyzed prior to release.

Calcium carbonate cookoff Calcium carbonate reacts with acidic gases produced by explosive detonations. It has the additional advantages of reducing sound, thermal shock, collatoral damage and debris spreading. For this study the energetic component(s), surrounded by $CaCO_3$ in a sealed

pressure vessel, is heated to detonate the explosive. The detonation products react with the $CaCO_3$ to neutralize the acid gases formed from the oxidation of the heteroatoms present in the component.

Forty tests were completed resulting in the disposal of 179 actuators. Twenty four of these were SCWO tests, and the remaining sixteen were split equally between NaOH and $CaCO_3$ experiments.

The results are briefly summarized as follows:

- All three of the processes destroyed the explosive hazard of the energetic components.
- Batch SCWO at 500°C achieved essentially complete oxidation of the organics, forming carbon dioxide, water, nitrogen, and metal oxides. Further development is desirable for operating parameter optimization.
- Calcium carbonate demonstrated the ability to act as a thermal sink by moderating the rapid thermal release from the detonations. However, the tests were not run with sufficient oxidizing agent to achieve complete oxidation.
- Sodium hydroxide scavenged the carbon dioxide produced by the reaction. The large vessel used for the hydroxide studies limited the sensitivity of the measurements that could be made.

The results from this preliminary examination of these three processes for energetic component disposal are very encouraging. Further testing is desired to optimize operating parameters and better understand how to apply the processes.

2.0 Introduction

Over the years Sandia has been asked to identify destruction options for explosive components and munitions that are particularly difficult to treat. The list of items includes artillery rounds containing armor and antipersonnel shaped charges, chemical filled munitions and small energetic components. Energetic components, such as the detonators and actuators commonly used in weapon systems, are especially difficult to dispose of because they contain a variety of hazardous, reactive materials. Although such components are relatively small, they are usually inventoried in large numbers and thus can represent a large disposal problem in the aggregate. In addition, components containing substantial quantities of sensitive, primary explosives (including some with toxic lead and mercury compounds) are often difficult to handle safely.

Traditional disposal options (e.g., open burning, open detonation and incineration) for such components are limited because of environmental concerns related to atmospheric release of toxic gases and soil contamination by heavy metals. The study described in this report was therefore undertaken to determine the effectiveness of alternative, environmentally sound, disposal options. Further, the small size of individual components enables us to optimize the various process parameters of these options while carrying out bench scale experiments in a laboratory setting. In this way we can predict how these disposal alternatives can be scaled for application to large munition items in the DoD demilitarization inventory.

In the course of brainstorming potential destruction methods, the following three concepts were generated that, to our knowledge, have never been previously applied to component disposal.

- Supercritical water oxidation (SWCO) batch reactor
- Sodium hydroxide solution (NaOH) scrubbing (base hydrolysis), and
- Calcium carbonate ($CaCO_3$, limestone) cookoff

These processes were chosen based on their potential for producing a clean solid residue and a minimum release of toxic gases after component detonation. In addition, each concept has specific long-range application potential such as use on shape charges, component assemblies or chemical filled rounds. None of these disposal methods requires component disassembly prior to application, thus enhancing personnel safety.

The effectiveness of these three processes for disposal of small energetic components is examined in this study. The experimental program, using representative Sandia components, is described followed by test results and analytical measurements of gaseous and solid emissions from the tests. The conclusions we draw from this study are summarized in section 6.0.

3.0 Experimental Program

All of the testing described in this report was performed on MC1061 and MC1981 hot wire explosive actuators. Each actuator contains 250 mg lead styphnate and is about 0.5 inches in diameter by 1.0 inches long. The test results reported here provide data to aid in forecasting the potential use of these new destruction concepts. They do not in themselves prove a technology will or will not work. Test conditions for the three destruction methods are briefly described in this section of the report.

3.1 Batch SCWO Processing

The SCWO treatment process uses water above its critical point [374 °C, 3200 psia (22.1 MPa)] and an oxidizer to destroy hazardous organic materials. The process, which has been widely demonstrated using both batch and flow reactor configurations, has proven to be quite effective in destroying a variety of waste streams (Ref. 1). A batch reactor was chosen for the present study because it offers the advantage of treating several components simultaneously and without disassembly. As many as eight explosive actuators, each containing 250 milligrams of lead styphnate, were placed in a 325 cubic centimeter Inconel 625 pressure vessel with water and oxidizer and heated to supercritical conditions. The auto-ignition temperature for lead styphnate is around 275 °C at a slow heating rate, thus the actuators detonate before the vessel reaches supercritical conditions. The detonations are completely contained inside the vessel. After detonation of the explosive, the explosive by-products as well as actuator material, brass, cardboard and plastics, are taken to supercritical conditions and oxidized. The reaction products are CO_2, H_2O, N_2, and metal oxides. Several parameters were investigated in this series of experiments. The specifics are discussed in Section 5.1. The parameters of interest in this process include heating rate, temperature, pressure, and the quantity of oxidizer added to the reactor. Two different oxidizers, hydrogen peroxide and air, were examined. Conditions for the SCWO testing described in this paper are summarized in Table 1.

The quantities of air are listed in moles. Hydrogen peroxide is listed in grams of 30 weight percent solution. "Start" indicates the oxidizer was added at the beginning of the test before heating began. "ND" means the detonation could not be detected in the pressure and temperature data. No data were collected on tests 8-1 through 8-4 due to a computer malfunction.

Table 1 Batch SCWO Test Conditions

Test	No. of	Water	Oxidizer		Temperature - C			Pressure - psia		
No.	Act	Amt.-g	Form	Amt.	Ox. Add.	Peak	Det.	Ox. Add.	Peak	Det.
1-1	1	40.3	None			460	225		3800	
2-1	8	48.6	Air	0.21 M	450	470	218	4600	5450	290
2-2	8	21.8	None		450	450	210	3100	3500	300
2-3	1	48.6	H_2O_2	3 g	Start	460	ND	Start	4540	ND
2-4	1	48.6	H_2O_2	3 g	Start	460	ND	Start	4575	ND
5-1	8	19.8	Air	1.4 M	400	510	220	2000	6400	400
5-2	4	19.8	Air	1.4 M	Start	390	230	Start	6400	3200
5-3	4	12.5	Air	1.4 M	450	700	240	1600	6100	400
5-4	8	12.5	Air	1.4 M	Start	460	230	Start	6500	3200
6-1	7	17.8	Air	1.28 M	400	460	215	2000	6100	300
6-2	5	17.8	Air	1.28 M	Start	410	225	Start	6200	3000
6-3	5	11.3	Air	1.28 M	460	575	220	1600	5900	300
6-4	7	11.3	Air	1.28 M	Start	460	225	Start	6100	3000
7-1	5	17.8	None		Vessel	Leaked		Vessel	Leaked	
7-2	7	17.8	Air	1.28 M	Start	410	210	Start	6200	2800
7-3	7	11.3	None		Vessel	Leaked		Vessel	Leaked	
7-4	5	11.3	Air	1.28 M	Start	470	200	Start	6300	2800
8-1	7	91.0	H_2O_2	61.3 g	Start	No	Data	Start	No	Data
8-2	5	91.0	H_2O_2	61.3 g	Start	No	Data	Start	No	Data
8-3	5	0	H_2O_2	61.3 g	Start	No	Data	Start	No	Data
8-4	7	0	H_2O_2	61.3 g	Start	No	Data	Start	No	Data
9-1	7	17.8	Air	1.28 M	410	420	150	2100	6000	20
9-2	5	17.8	Air	1.28 M	410	520	160	2000	6000	50
9-3	7	11.3	Air	1.28 M	410	530	200	1800	6000	40

3.2 Sodium Hydroxide Base Hydrolysis

Base hydrolysis, employing a solution of sodium hydroxide, is used as a desensitization and disposal technique for energetic materials (Ref. 2). Chemical reaction with a strong base is also widely used for scrubbing incineration produced acid gases. The proposed process takes advantage of these characteristics of a base in an effort to minimize the hazardous products produced when an explosive component is detonated. To employ the process, the component is functioned (detonated) electrically while immersed in NaOH solution contained in a pressure vessel. In this way, detonation products (solid residue and gases) are contained and hydrolyzed prior to release. The parameters of interest include initial NaOH solution concentration and the containment vessel temperature and pressure. The NaOH test conditions are summarized in Table 2. The experiments are discussed in Section 5.2.

Detonating munitions in a bath of sodium hydroxide has potential application to destruction of both chemical filled munitions as well as munitions containing shape charges. The sodium hydroxide can neutralize many chemical fills and can safely absorb the energy from a shaped charge.

3.3 Calcium Carbonate Cookoff

Calcium carbonate reacts with the acidic gases produced by explosive detonation events. This technique provides the additional advantage that the limestone can reduce sound, collateral damage, and the spreading of debris. For this study, the component, surrounded by $CaCO_3$ in a sealed

Table 2 Sodium Hydroxide Test Conditions

Test ID	No. of Act.	Vessel Contents		Peak Temp. -°C	Peak Press. -psia
		NaOH-ml (25%)	Atmos. (psia)		
NaOH-1	1	None	Air (14.7)	80	31.4
NaOH-2	1	None	Air (14.7)	71	32.2
NaOH-3	1	200	Air (14.7)	18	?
NaOH-4	1	200	Air (14.7)	14	15.8
NaOH-5	1	200	Air (14.7)	17	15.3
NaOH-6	1	200	Air (200)	15	211
NaOH-7	1	200	Air (200)	18	210
NaOH-8	1	200	Air (1.3)	15	1.7

pressure vessel, is rapidly heated to detonate the explosive. The $CaCO_3$ cookoff test conditions are summarized in Table 3. The calcium carbonate particle size distribution for all of the tests was broad and <25 mesh. The experiments are discussed in Section 5.3.

An important potential application for this process is the destruction of particularly hazardous munitions such as those containing shape charges. A shape charge could be expected to detonate harmlessly in a $CaCO_3$ bed since the resultant molten metal jet would dissipate in the $CaCO_3$ powder. The copper from the shape charge jet and the steel from the shape charge housing, as well as all other solid material, may be recycled by sifting the $CaCO_3$.

Table 3 Calcium Carbonate Test Conditions

Test ID	No. of Act.	Vessel Contents			Temperature - °C		Pressure - psia	
		$CaCO_3$ -g	Atmos. (psia)	Water -g	Peak	Det.	Peak	Det.
$CaCO_3$-1	1	34	helium (14.7)		420	270	65	15
$CaCO_3$-2	1	66	helium (14.7)		420	280	95	10
$CaCO_3$-3	1	34	helium (14.7)		420	280	50	10
$CaCO_3$-4	1	66	helium (14.7)		410	290	145	50
$CaCO_3$-5	8	None	helium (14.7)		325	140	165	12
$CaCO_3$-6	8	filled vessel	helium (14.7)		325	240	200	45
$CaCO_3$-7	8	filled vessel	helium (14.7)	5.0	340	240	800	250
$CaCO_3$-8	8	filled vessel	air (1000)		340	220	2250	1800

4.0 Analytical Procedures

After some tests an overgas sample was withdrawn from the test vessel. This gas sample along with the liquid and solid residue from the test vessel were taken to the chemistry laboratory for analysis. The analytical procedures applied to these samples are briefly described below.

4.1 Overgas Analysis.

A sample of the overgas at room temperature was transferred into a sample bottle at a pressure of ≤ 1 atmosphere. The sample was expanded into a septum-capped, evacuated chamber and a 100 μl sample was withdrawn into a gas-tight syringe. The syringe needle was pushed through the injection port of a HP5890A gas chromatograph having a HP5970 mass selective detector. The needle was flushed by the carrier gas for 2 minutes and then the sample was injected onto a 30 m long, 0.32 mm diameter, GasPro™ gas separator column (a bonded PLOT column). The injection port was kept at 260 °C and the column was ramped from 30 °C to 260 °C at 10 °C/min. Most common gases were resolved. The largest molecules detected were C_6 hydrocarbons.

4.2 Vessel Contents Analysis

Samples of the reactor liquids (or solid $CaCO_3$) that purposefully included any precipitates present were dissolved in 5% HNO_3 and then diluted to 2% HNO_3 with high purity water. Further serial dilutions were performed depending on the concentration of the analytes and the method of analysis. Metals were analyzed on either a Perkin Elmer P1000 inductively coupled plasma-atomic emmission spectroscopy (ICP-AES) or a Fisons PlasmaQuad, PQS, inductively coupled plasma-mass spectrometer (ICP-MS).

5.0 Test Program Results

5.1 Supercritical Water Oxidation

A total of 134 actuators were destroyed in 24 separate tests using the SCWO batch reactor. The number of actuators used for each test ranged from one to eight. The primary test objective was complete oxidation of the organic products. Parameter optimization to minimize reactor volume and corrosion were secondary objectives.

The actuators were loaded in the batch reactor vessels with the desired amount of water, then the vessels were sealed and leak tested. In some tests the actuators were submersed in the liquid, while in others they were supported above the liquid. There was no evidence that the actuator position made any difference. Air, which was either added before the test or after the vessel reached the desired temperature, was generally used as the oxidizer. Hydrogen peroxide (H_2O_2) was added to the initial water fill on a few tests as an alternate oxidizer. Previous tests have shown that the hydrogen peroxide decomposes very rapidly to water and oxygen at about 170°C. Consequently, the oxidizer in either case was gaseous oxygen.

The vessels were heated with external band heaters, causing a simultaneous pressure increase as the water evaporated. Reactor conditions were recorded by a Teledyne Taber pressure transducer and a thermocouple inside the vessel. Figure 1 shows typical pressure and temperature histories for a reactor with no reacting materials.

The actuator detonations were usually apparent in the temperature and pressure data. Several detonations appear as steps in Figure 2. The detonations were less apparent when the reactor did not have an initial air overpressure. This is shown in Figure 3, where there was no pressure response

to the first actuator detonation, and the temperature appeared to drop each time an actuator detonated. This drop in temperature may be due to the fact that the vessel was not at a uniform temperature, and there was still a liquid phase that could be splashed around the vessel during the detonation.

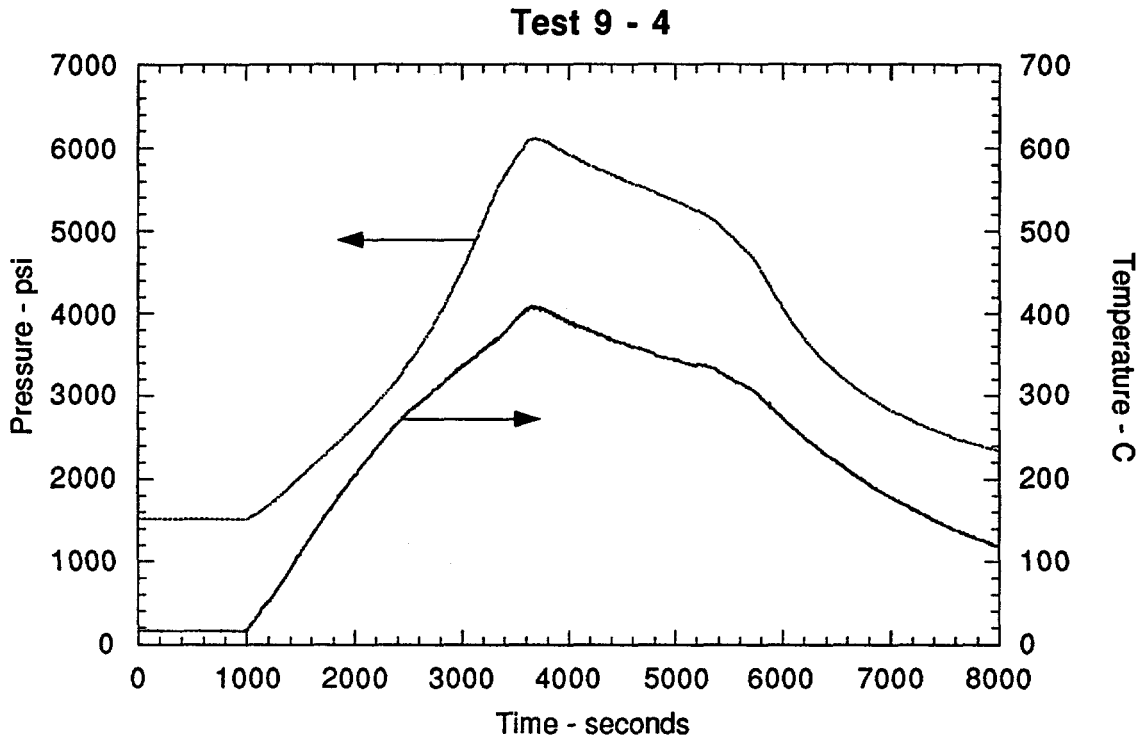

Figure 1. Pressure and temperature histories for SCWO reactor with only water.

This theory is supported by data from a second thermocouple located near the top of the reactor shown in Figure 4. It showed much smaller fluctuations, but the two thermocouples tended to converge with each detonation.

The test variables were the amount of oxidizer (or the number of actuators with a fixed amount of oxidizer), temperature (~390°C to ~520°C), time at temperature (1 to 60 minutes), and the time at which the oxidizer was added. Table 4 summarizes the analytical test results. The testing succeeded in identifying conditions that fully oxidized the actuator products. However, there was insufficient testing to determine the influence of each variable.

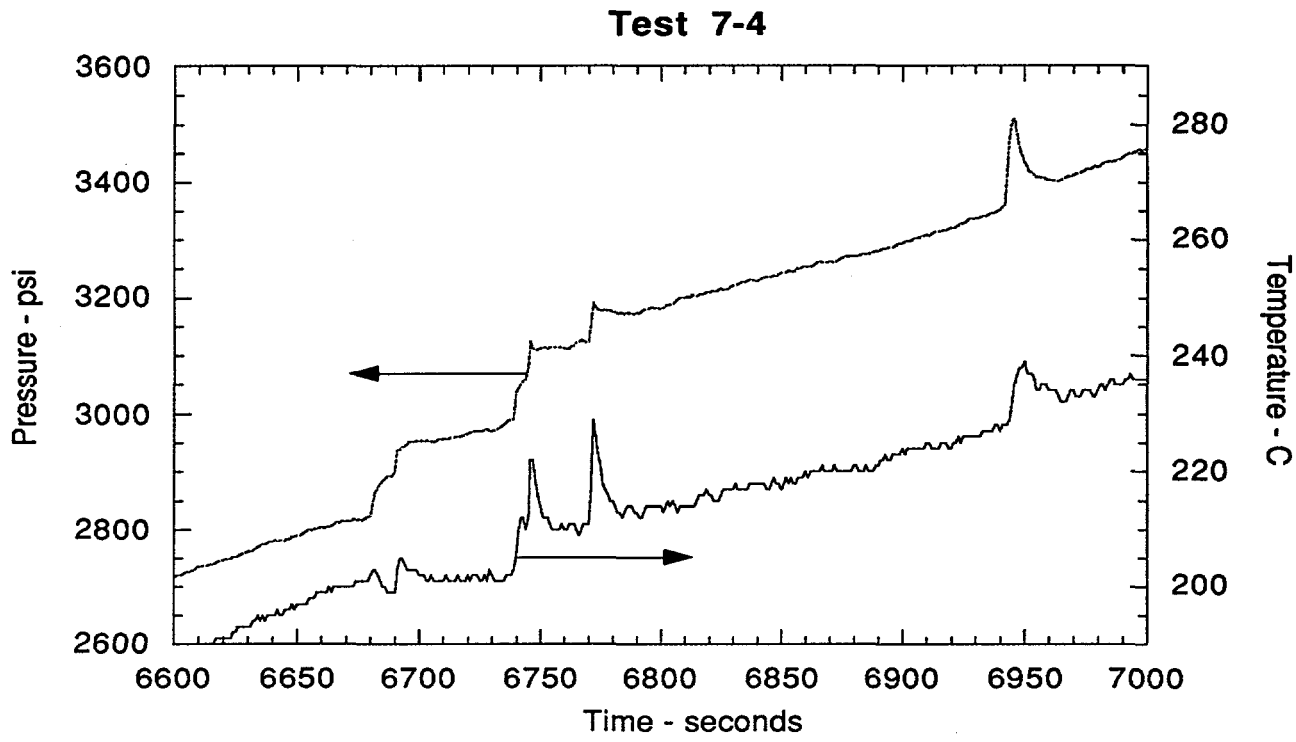

Figure 2. SCWO pressure and temperature histories during actuator detonations with oxidizer.

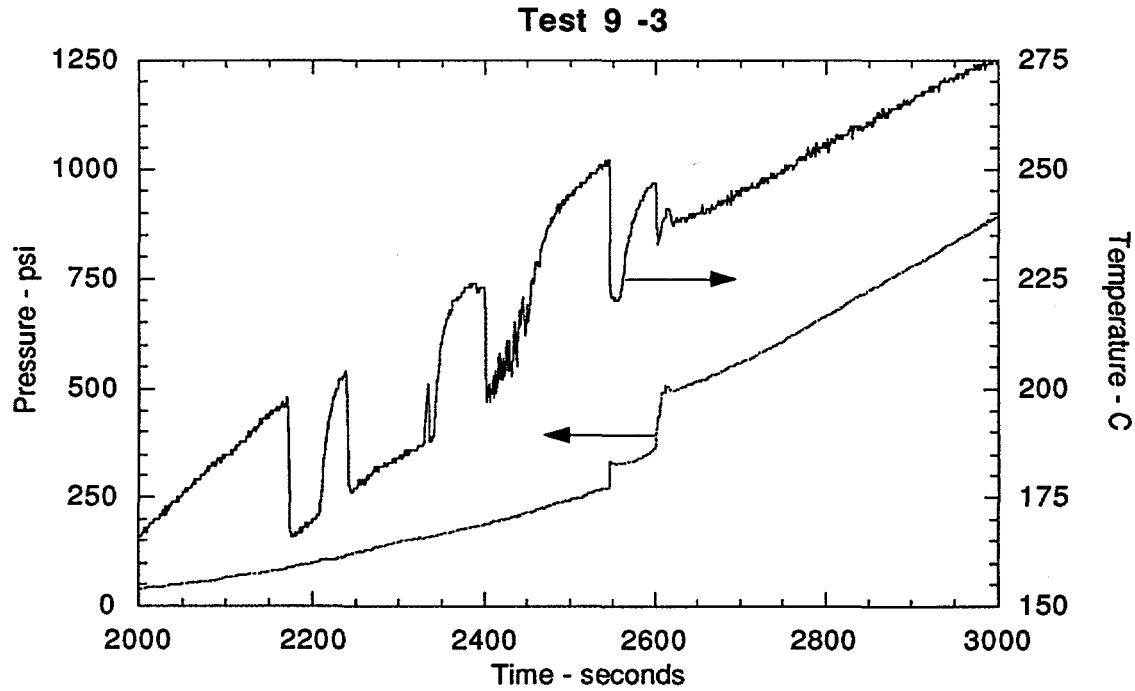

Figure 3 SCWO pressure and temperature histories during actuator detonations without oxidizer.

The most important variable was the amount of oxidizer. The explosive contains its own oxidizer, but additional oxidizer is needed for complete oxidation. The actuators also contain paper packing material and possibly plastic or epoxy compounds. The effluent from the initial tests had greater than 10,000 ppm total organic carbon (TOC), which came primarily from these non-explosive compounds. The effluent was dark brown, had an oily appearance, and contained black particulate. The pH was slightly basic. The overpressure had high levels of low molecular weight hydrocarbons, (mostly alkenes C_2-C_6 + benzene), which are typical products of organic pyrolysis. It also had an obnoxious odor. The actuator housings were coated with a thick, black, oily residue. Nevertheless, the explosive was fully destroyed.

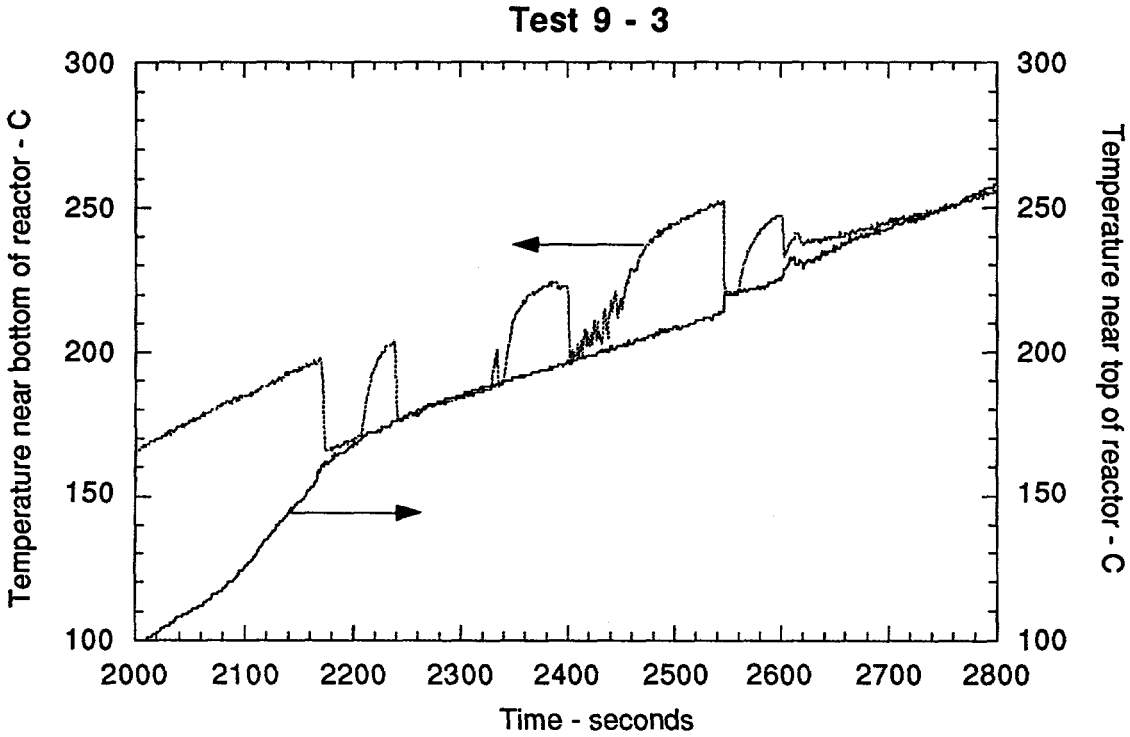

Figure 4. SCWO temperature histories at reactor ends during actuator detonations.

On later tests, the amount of oxidizer was significantly increased resulting in essentially complete destruction of all organic compounds. On test 9 - 2, with approximately 0.3 moles of O_2 for five actuators, the effluent was clear with 45 ppm of TOC and pH of 6. The overpressure after this test consisted of clean wet air with increased CO_2 levels. There was no noticeable odor, and the actuator housings were clean and shiny. Test 9 - 1, which had 0.3 moles of O_2 for seven actuators, had 670 ppm TOC, a slight greenish-gray tint, and a pH of 7. This suggests that there was not quite enough oxygen. Test 9 - 3 also had seven actuators, but had 5 % less oxidizer. It had 1200 ppm TOC with a pH of 10, suggesting even more oxygen deprivation. Note, however, that 9 - 3 had less water so the same mass of carbon would result in a 50 % higher TOC concentration.

When the oxidizer was present from the start of the test, the oxidation occurred at the time of detonation and during the heatup. It was essentially complete by the time the reactor reached the

Table 4 SCWO Test Series Analytical Results

Test No.	No. of Act.	pH	TOC ppm	Metals - ppm Cr	Ni	Mo	Pb	Gas
1-1	1	8	865					Mixed Low MW HC
2-1	8	8		0.003	N/D	16, 23	2	
2-2	8	8		0.004	N/D	5	0.9	
2-3	1	8	2500	0.002	1.1	0.4	0.8	
2-4	1	8	2700	0.003	N/D	0.4	1.2	
5-1	8		>4000					Trace benzene
5-2	4		1260					Clean wet air
5-3	4		209					Clean wet air
5-4	8		1470					
6-1	7							Clean wet air
6-2	5							Clean wet air
6-3	5							Clean wet air
6-4	7							Clean wet air
9-1	7	7	671					
9-2	5	6	45					
9-3	7	10	1178					

Note: Blank spaces in the table indicate samples that were not analyzed.

desired final temperature and pressure. Figure 5 shows no sign of rapid oxidation other than a small temperature spike between 7,500 and 8,000 seconds at about 300°C. By contrast, adding the oxidizer after the system was heated resulted in rapid reaction with sudden jumps in temperature as shown in Figures 6 and 7. This test, 9-3, included two thermocouples, one near the top of the vessel and

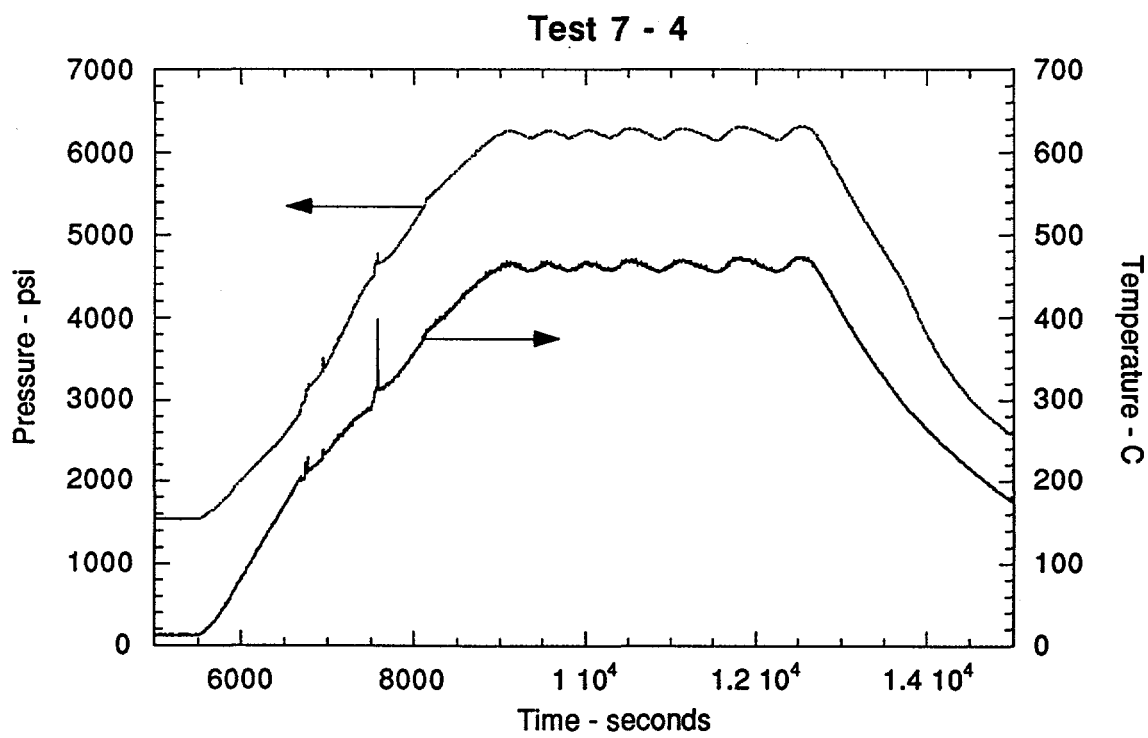

Figure 5. SCWO pressure and temperature histories with oxidizer added at start.

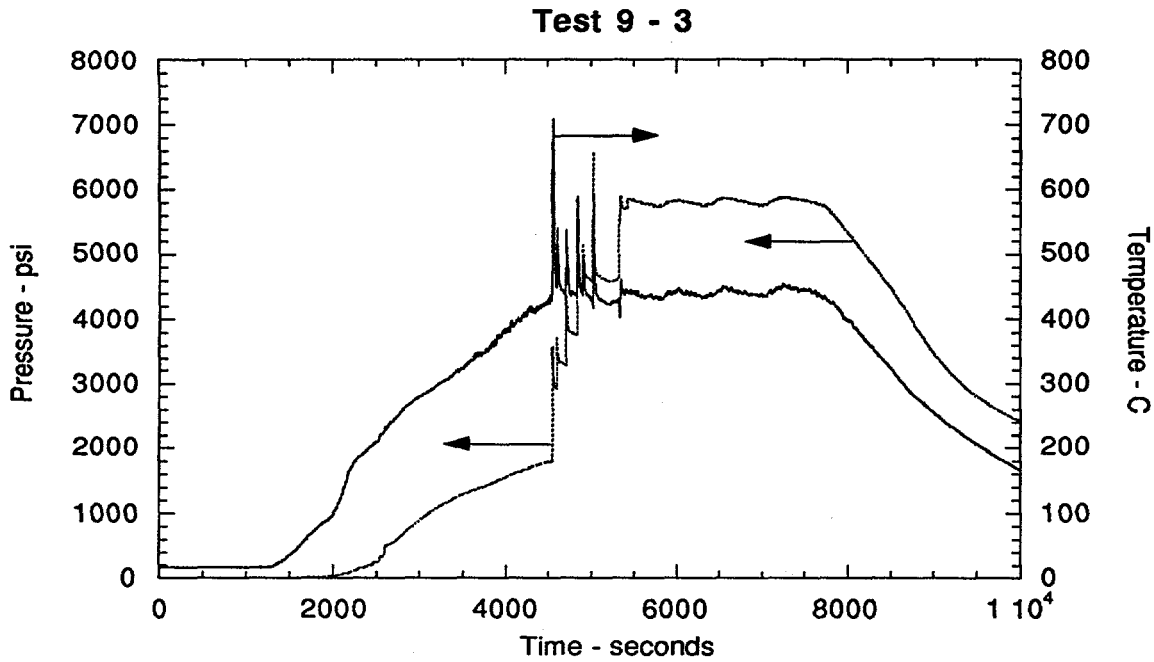

Figure 6. SCWO pressure and temperature histories with oxidizer added during the test.

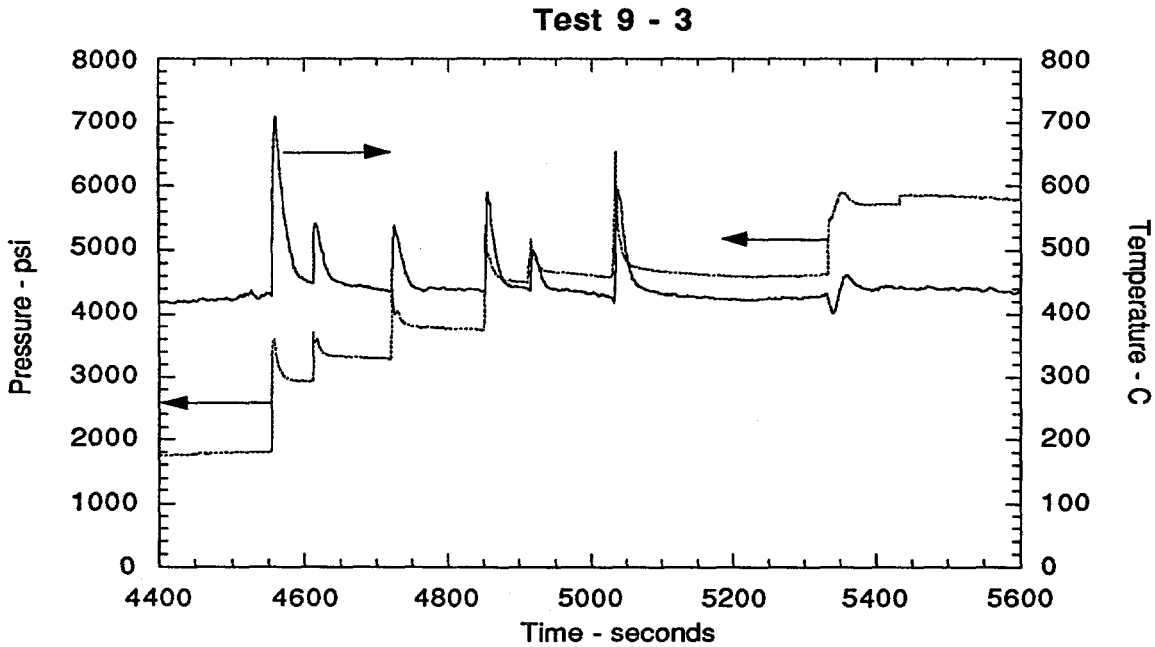

Figure 7. SCWO pressure and temperature histories with expanded time scale during oxidizer addition.

one near the bottom. Most tests had only the one near the bottom. The jumps in temperature were not as large at the bottom of the reactor as shown in Figure 8 . Apparently the air reacted

immediately as it entered the top of the vessel, creating a local hot spot. This rapid heating made it difficult to control the temperature and consequently, the influence of temperature as an operating parameter is difficult to extract from the tests. Since reaction kinetics are such a strong function of temperature, even a short spike may play a significant role in determining the total destruction efficiency. These temperature jumps could be reduced by restricting the rate of air flow into the reactor, but our test set up does not provide that level of control.

Corrosion of the reactor does not appear to be a problem because the pH of the effluent is almost neutral. Concentrations of chromium, nickel, and molybdenum in the liquid effluent were very low. Often, dark sludge formed on the bottom of the reactor. It was not analyzed directly, but was qualitatively included in the liquid analysis. The residue appeared to contain metal oxides including lead from the explosive, zinc and copper from the actuator housing, and possibly corrosion products from the reactor.

In summary, with sufficient oxidizer all of the detonation products of the actuators can be fully oxidized at supercritical conditions. The optimum temperature for the reaction has not been determined, but 500°C is sufficient.

5.2 Sodium hydroxide base hydrolysis

Six tests were conducted with NaOH using one actuator in each. Two reference tests were done in the same vessel without NaOH. Table 5 shows the analytical test results. The volume of the vessel

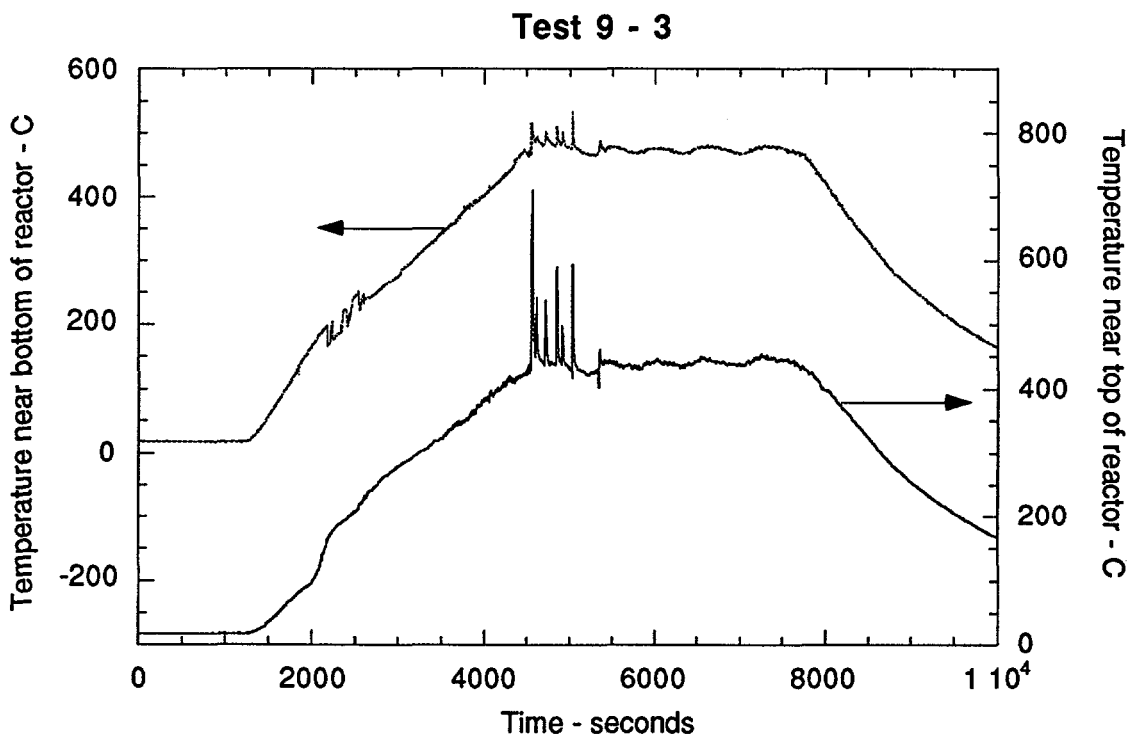

Figure 8. SCWO temperature histories at reactor ends .

was about ten times larger than that used for the SCWO and $CaCO_3$ tests. This and other differences make it difficult to compare results from the NaOH tests with the other tests.

The actuators were suspended in the liquid and detonated with an electrical signal in their normal manner. The reference tests showed trace amounts of organic carbon in the overpressure, while the tests with NaOH produced clean wet air. With the NaOH, there was no CO_2 in the gas. It appears from these tests that sodium hydroxide is effective at scrubbing the gaseous actuator products. Again, if excess oxidizer were used, the products should be clean with CO_2-free air above a solution/suspension of metal oxides. Some of the reactor metals were found in acid digests of the solution, but only lead exceeded 100 ppm.

Table 5 Sodium Hydroxide Test Series Analytical Results

Test ID	pH	Metals - ppm					Gas
		Cr	Ni	Mo	Pb	Other	
NaOH-1	N/A						Trace organics
NaOH-2	N/A						Trace organics
NaOH-3	>13	68	N/D		232		Wet air, no CO_2
NaOH-4	>13	88	N/D		224		Wet air, no CO_2
NaOH-5	>13						Wet air, no CO_2
NaOH-6	>13						
NaOH-7	>13						
NaOH-8	>13						

Note: Blank spaces in the table indicate samples that were not analyzed.

5.3 Calcium carbonate cookoff

Eight tests were performed in the calcium carbonate cookoff series. Seven tests were conducted with commercial oyster shell derived $CaCO_3$, and one reference test (test 5) was conducted in one atmosphere helium without $CaCO_3$. The $CaCO_3$ acts to control the exothermic reaction; first, by providing a local heat sink and second, by capping the ultimate local temperature. $CaCO_3$ decomposes endothermically at 825 °C to CaO and CO_2. Additionally any acidic gases formed by the oxidation of heteroatoms [phosphorous (P), sulfur (S), etc.] would be neutralized by the basic carbonate.

Twenty eight actuators were tested with calcium carbonate and eight actuators were used in the helium atmosphere reference test. One actuator each was used for Tests 1 - 4 and eight actuators each were used for tests 6 - 8. Table 6 shows the analytical test results. The actuators were buried in the $CaCO_3$ inside vessels identical to those used for the SCWO batch reactor tests. The vessels were heated to between 325°C and 420°C. All actuators detonated between 240°C and 290°C. For the tests with eight actuators, one vessel had dry $CaCO_3$, the second had a small amount of water added to the $CaCO_3$, and the third had $CaCO_3$ with a 1000 psi air overpressure. This amount of air was chosen arbitrarily and was less than needed to fully oxidize the organic compounds.

The post test overpressure from the reference vessel had a mixture of low molecular weight hydrocarbons typical of pyrolysis, mostly alkenes, and a strong burnt odor. Both of the vessels with $CaCO_3$, but no air, had similar hydrocarbons but not as much. The odor from the vessel with dry $CaCO_3$ was different and more foul than that from the reference vessel. The wet $CaCO_3$ had an

odor like the reference vessel but not as strong. The vessel with the air overpressure had very little odor, but the gas was not analyzed. These experiments suggest that the calcium carbonate had some scrubbing benefit, but air was most beneficial. Had sufficient oxidizer been used for complete oxidation, the neutralizing effect of the $CaCO_3$ would have been utilized.

Table 6 Calcium Carbonate Test Analysis Results

Test ID	Metals - ppm							Gas
	Al	Cr	Fe	Ni	Mo	Pb	Other	
$CaCO_3$-1	30.21	N/D	41.32	N/D	N/D	137.01		
$CaCO_3$-2	26.21	N\D	37.91	N/D	6.67	52.11		
$CaCO_3$-3	30.52	0.13	30.65	0.12, 1.3	0.27	71.8	Sr 38, Mn 20	Mixed low MW hydrocarbons typ. of pyrolysis: mostly alkenes
$CaCO_3$-4	32.8	1.1	47.4, 25.4	10	2.2	167, 158.93	Sr 3100, Mn 1600	
$CaCO_3$-5								Mixed low MW hydrocarbons typ. of pyrolysis: mostly alkenes
$CaCO_3$-6								Mixed low MW hydrocarbons typ. of pyrolysis: mostly alkenes
$CaCO_3$-7								Mixed low MW hydrocarbons typ. of pyrolysis: mostly alkenes
$CaCO_3$-8								

Note: Blank spaces in the table indicate samples that were not analyzed.

Figures 9 and 10 show the pressure and temperature data for the reference and dry vessels respectively. Interestingly, the eight actuators detonated simultaneously.

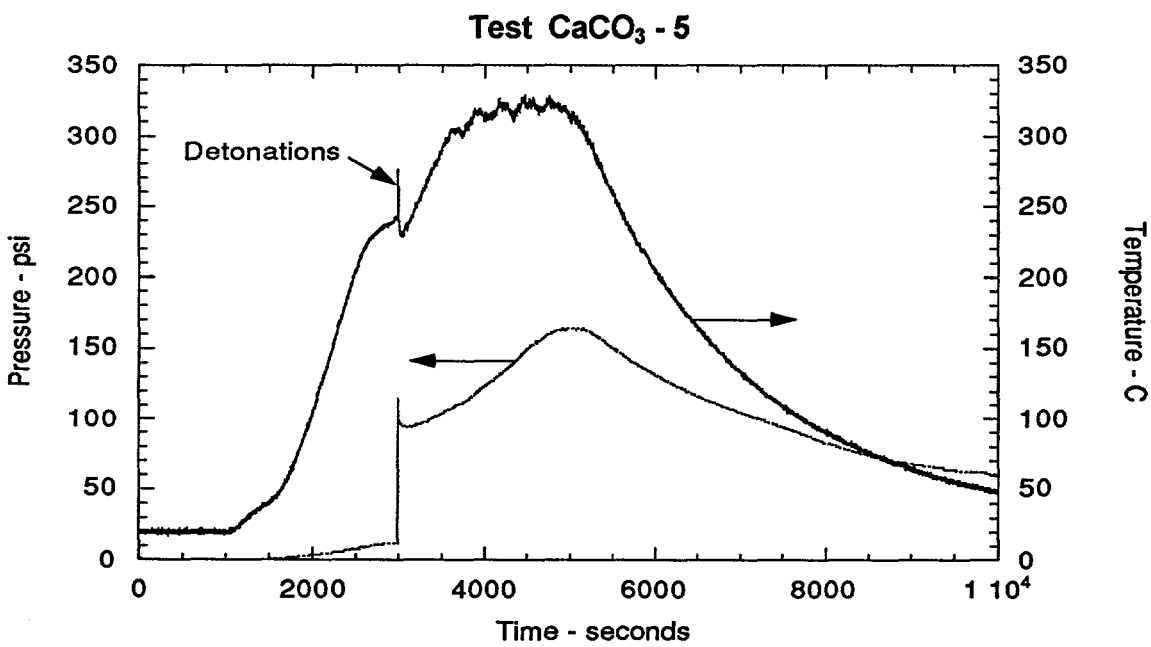

Figure 9. Pressure and temperature histories for $CaCO_3$ reference test.

The vessels with $CaCO_3$ showed similar behavior. Figure 11 shows data for the $CaCO_3$ with air overpressure. The $CaCO_3$ absorbed the thermal energy from the actuators; so, Figures 10 and 11 do not show a temperature increase like Figure 9, but the jump in pressure is still apparent.

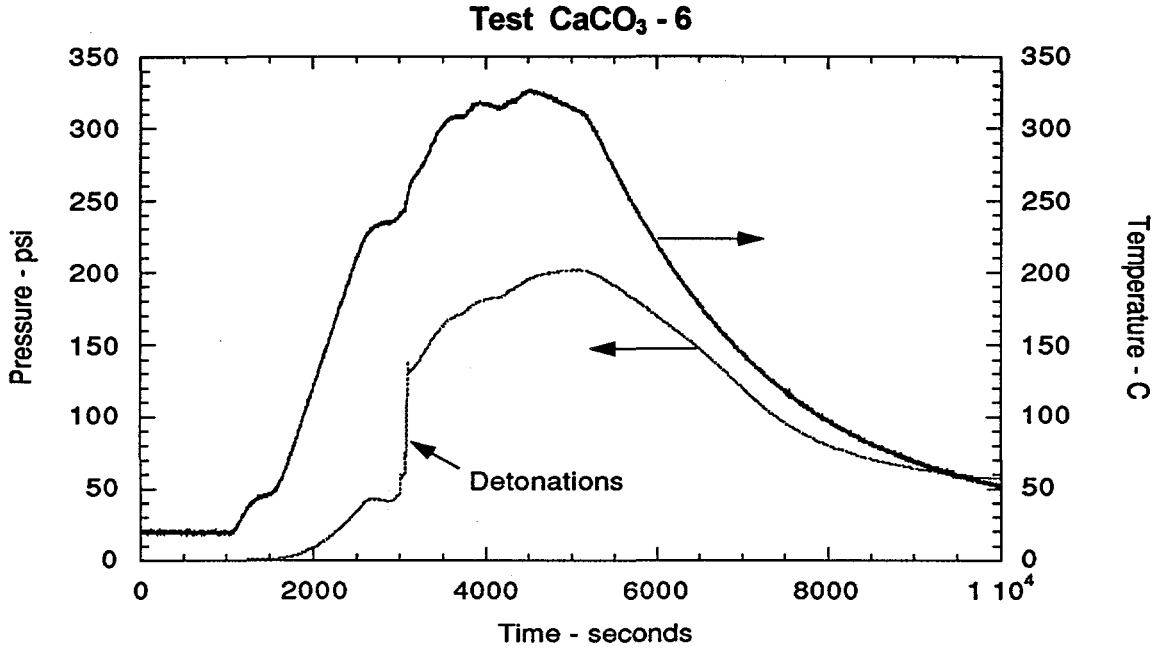

Figure 10. Pressure and temperature histories for the dry $CaCO_3$ test.

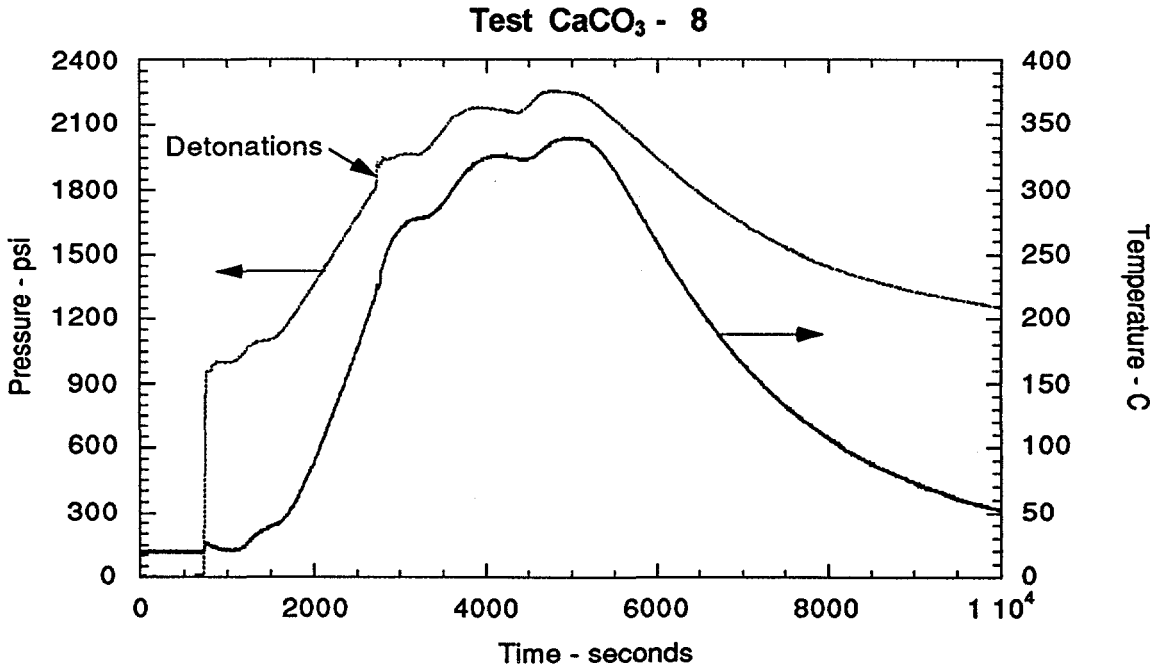

Figure 11. Pressure and temperature histories for $CaCO_3$ test with air overpressure

6.0 Conclusions and Recommendations

All three of the processes destroyed the explosive hazard of the energetic components. With sufficient oxidizer, batch supercritical water oxidation destroys the energetic and the organics, forming carbon dioxide, water, nitrogen, and metal oxides. Further development of this process is desirable to optimize the operating parameters. Oxidation of detonation products was essentially completely acheived in tests at, and above, 500°C but a lower temperature may be sufficient. Reactor corrosion was minimal.

The calcium carbonate tests were not run with sufficient oxidizing agent to yield conditions of complete oxidation. We assume the material would fully neutralize acids formed from the oxidation of the heteroatoms present in the component. The calcium carbonate did demonstrate its ability to act as a thermal sink by moderating the rapid thermal release from the detonations. Specific measurement of noise, fragment and blast mitigation were not made.

Comparing the effects of caustic sodium hydroxide to the calcium carbonate, we see that the hydroxide is able to scavenge the carbon dioxide produced by the reaction. The large vessel used for the hydroxide studies limited the sensitivity of the measurements that could be made. Presumably, the base would neutralize any acid formed, scavenge carbon dioxide and precipitate most metals as their hydroxides. The disadvantages of using hydroxide solutions instead of calcium carbonate are that the material itself is hazardous and the solution will not mitigate the shock of detonation.

These preliminary experiments have successfully demonstrated that SCWO, sodium hydroxide base hydrolysis and calcium carbonate cookoff are promising technologies for destruction of energetic components. Continuation of these experimental programs is strongly recommended for all three processes as resources become available in the future.

7.0 References

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DISTRIBUTION

Curtis Anderson
U.S. Army Armament Research, Development & Engineering Center
SMCAR-AES-P
Bldg 321
Picatinny Arsenal, NJ 07806-5000

Ed Ansell
U.S. Army Defense Ammunition Center and School
USADACS
ATTN: SMCAC-TD
Savanna, IL 61074-9639

Alan Caplan
U.S. Army ERDC
SCBRD-EN (Demil)
Bldg E4405, Rm 216
Aberdeen Proving Ground, MD 21010-5401

Joe Craten
Acting Deputy U.S. Army Garrison
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Director Safety Health & Environment
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Aberdeen Proving Ground, MD 21005-5001

Michael Duggan
U.S.Army NSCMP
ATTN: AMCPM-NSP
Aberdeen Proving Ground, MD 21010-5401

Ray Goldstein
U.S. Army Armament Research, Development & Engineering Center
SMCAR-AES-P
Bldg 321
Picatinny Arsenal, NJ 07806-5000

Jerry Hawks
U.S. Army ERDC
SCBRD-EN (Demil)
Bldg E4405, Rm 216
Aberdeen Proving Ground, MD 21010-5401

Charles Heyman
U.S. Army NSCMP
ATTN: SFAE-CD-NM
Bldg E4405
Aberdeen Proving Ground, MD 21010-5401

Wayne Jennings
U.S. Army Chemical Materiel Destruction Agency
USACMDA
ATTN: SFIL-NSP
Aberdeen Proving Ground, MD 21010-5401

Solim S. Kwak
U.S. Army Defense Ammunition Center
ATTN: SIOAC-TDS
Savannah, IL 61074-9639

Col Edmund W. Libby
U.S. Army NSCMP
ATTN: SFAE-CD-N
Bldg E4405
Aberdeen Proving Ground, MD 21010-5401

Crane Robinson
U.S. Army Armament Research, Development & Engineering Center
SMCAR-AES-P
Bldg 321
Picatinny Arsenal, NJ 07806-5000

Robert Shaw
U.S. Army Research Office
Research Triangle Park, NC 27709-2211

Warren Taylor
U.S. Army NSCMP
ATTN: SFAE-CD-NM
Bldg E4405
Aberdeen Proving Ground, MD 21010-5401

James Wheeler
U.S. Army Defense Ammunition Center and School
USADACS
ATTN: SMCAC-TD
Savanna, IL 61074-9639

John W. Mikel
Division Head, Ordnance Engineering
Weapons Quality Engineering Center
Concord Naval Weapons Station
10 Delta Street
Concord, CA 94520-5100

Peter Rivard
Weapons Quality Engineering Center, In-Service Engineering Branch
Code: 354
Concord Naval Weapons Station
10 Delta Street
Concord, CA 94520-5100

Michael Shelton
Weapons Quality Engineering Center
Concord Naval Weapons Station
10 Delta Street
Concord, CA 94520-5100

Gopal Gupta & K. S. Ahluwalia
Foster Wheeler Development Corporation
8 Peach Tree Hill Road
Livingston, NJ 07039

George Y. Wu
Program Manager, Environmental Department
Naval Facilities Engineering Service Center
Code: ESC 45
1100 23rd Avenue
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